

**STUDIES ON SULFUR DIOXIDE REMOVAL USING
CALCIUM SILICATE AS SORBENT**

*A Thesis Submitted
in Partial Fulfilment of The Requirement
for the Degree of
Master of Technology*

by

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to the

**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

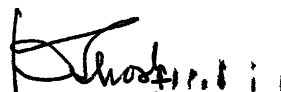
JULY, 1992

**TO
MY PARENTS**

CERTIFICATE

Certified that the work presented in this thesis entitled " STUDIES ON SULFUR DIOXIDE REMOVAL USING CALCIUM SILICATE AS SORBENT", by Arun Kumar Saxena has been carried out under my supervision and has not been submitted elsewhere for a degree.

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NOMENCLATURE

C_o	Inlet SO_2 concentration
C_{SO_2}	Concentration at any time t
d_p	Particle diameter
D	SO_2 Molecular diffusion coefficient
E	Activation Energy
k	Rate constant
l	Sand bed length
N	Number of moles
r	Rate of reaction
R	Universal gas constant
T_o	Temperature at the inlet to the reactor
u	Gas velocity
V_o	Gas flow rate
V	Volume of bed
X	Fractional SO_2 removal
X_f	Final fractional SO_2 removal

GREEK SYMBOLS

ϵ	Porosity of bed, fraction
ρ	Gas density
τ	Space time
μ	Gas viscosity

ABBREVIATION

Re	Reynold number
RH	Relative humidity
Sc	Scmidt number

ABSTRACT

In the present work an attempt has been made to study dry removal of sulfur dioxide in a laboratory scale set-up using calcium silicate as sorbent.

Experiments were conducted in a packed bed reactor at low temperature (100°C – 240°C). The test gas (SO_2 in air) was passed through the bed consisting of 1 gm sorbent dispersed per 50 gm sand ($D_{50} = 0.456\text{mm}$). Average space velocity of 1876/hr was maintained throughout the study. Effect of inlet SO_2 concentration, humidity of test gas, temperature on sulfation reaction were studied. The generalised empirical equations were obtained for different variables.

SO_2 removal was found to increase with increase in temperature (within the range studied). At higher SO_2 concentration, initial breakthrough occurred quickly. Increase of humidity increased the SO_2 removal. Order of reaction for $\text{CaSiO}_3/\text{SO}_2$ system has been obtained very close to 1.0. The variation of reaction rate constant with temperature in the Arrhenius form for the sulfation reaction was found to be $k = 5614.77e^{(-E/RT)}$ (l/mol)/hr, the activation energy, E being 199.04 cal/mol. Finally results obtained using the empirical equations have been found to reasonably corroborate with the experimental data.

1. INTRODUCTION

Due to increased population and increased industrial and other activities, vast quantities of potentially harmful waste products are being released into the atmosphere. This results in air pollution which affects the health and well-being of people, and causes damage to vegetation, crops, wildlife, materials, buildings and climate. The seriousness of air pollution for urban communities, as shown by effect of short-term pollution episodes or accidental releases of large quantities of a pollutant, has led ~~to pressure from both~~ national and local regulatory groups, which have largely been aimed at tackling local pollution problems. With a trend in the utility industry for life extension, retrofit technologies are likely to play an important role in any SO_2 emissions reduction of sulfur dioxide, a precursor for acid rain which threatens irreversible damage to sensitive aquatic and terrestrial ecosystems. Potential retrofit technologies include ~~flue gas~~ cleaning, wet or dry Flue Gas Desulfurisation (FGD), ~~conversion to fluidized bed~~, and dry sorbent injection. Compared to wet FGD processes, the dry calcium based processes will likely have lower SO_2 removal efficiencies (Offen, et al., 1987). However, ~~if~~ the sulfur content of the fuel is not very high, application of dry control process is likely to be an effective regulatory action.

Prior to 1980, removal of SO_2 from flue gas was usually carried out by a general technique that is wet scrubbing. This required considerable equipment involving high capital and operating cost to complete the process. This laid the development of dry scrubbing as low cost option. This method is found to be an effective control method for low sulfur fuel, since SO_2 removal in such dry FGD system is about 50 to 70 percent (Karlsson, et al., 1983; Miller, 1986). Also, it is 15 to 30 percent cheaper than the conventional wet scrubbing system (Samuel, et al., 1981; Offen, et al., 1987 and Egan, et al., 1986).

Much of the recent research and development in the area of dry FGD for SO_2 control has focused on improving SO_2 removal by developing (1) a better understanding of the process with commercially available sorbents; (2) modified or new sorbents; and (3) modified processes.

In the present work a packed bed reactor was used for studying the SO_2 removal. Calcium Silicate was used as the sorbent keeping in mind the possible usefulness of rock Wollastonite which contains about 99% Calcium Silicate. The sorbent was dispersed in sand bed and effect of various process variables on SO_2 capture were studied.

2. LITERATURE REVIEW

Sulfur dioxide is the most common gaseous air pollutant because of the wide occurrence of sulfur in fuels and mineral ores (Strauss, et al., 1973). Moreover the oxides of sulfur are probably the most wide-spread and most intensely studied of all anthropogenic air pollutants, and the problem of sulfur dioxide removal from the flue gases has been the subject of more research than any other gas purification process (Peavy, et al., 1986 and Khol, et al., 1979). Sulfur dioxide emission is, however, likely to grow unless suitable measures are taken to reduce the emission loads. In the present section, the occurrence of various oxides of sulfur in atmosphere, their sources, effects on environment and the present status of control technology has been discussed.

2.1 OCCURRENCE OF OXIDES OF SULFUR IN THE ATMOSPHERE

2.1.1 *Oxides Of Sulfur And Their Sources-*

In general there are six different oxides of sulfur in the atmosphere- Sulfur monoxide (SO), Sulfur dioxide (SO_2), Sulfur trioxide (SO_3), Sulfur tetraoxide (SO_4), Sulfur sesquioxide (S_2O_3), and Sulfur heptoxide (S_2O_7), (Peavy, et al., 1986). However only sulfur dioxide and sulfur trioxide are of prime importance in air pollution study, as they constitute more than 99% of total sulfur oxides emission (Stern, 1977). In the combustion of fossil

fuels the SO_2/SO_3 ratio is typically 40:1 to 80:1 (Work,et.al.,1981). Monitoring of sulfur compounds in the atomosphere is usually restricted to the dominant gas, sulfur dioxide.

The sources of sulfur oxides can be sorted as natural and anthropogenic. The natural sources are forest fires, Volcanic eruptions and conversion of hydrogen sulfide into sulfur dioxide in the atomosphere. Moreover, anthropogenic sources are of prime importance from the pollution control point of view. Out of all anthropogenic sources, it is found that the combustion of fossil fuels contribute about 80 percent SO_2 emission (Work,et al.,1981). Fuel combustion in stationary sources and industrial processes are the principal contributors of sulfur dioxides from human sources(Peavy,et al.,1986). However, there are some other sources also, like refining of petrolieum, the manufacturing of sulfuric acid, the burning of refuse, smelting of ores containing sulfur. A little amount is also contributed by transportation, because the sulfur content of gasoline is very low (about 0.03 percent by mass)(Peavy,et.al.,1986). A brief information regarding the contributors to SO_2 by various sources is given in Table 2.1.

Table 2.1

Various Sources And Their Contribution To Sulfur Dioxide

(Hunger Brauck, et al., 1968)

SOURCES	CONTRIBUTION TO SO ₂
Combustion of fossil fuel for power generation	46%
Other combustion of coal and petroleum products	32%
Smelting of ores	12%
Petroleum refinery	5.5%
Miscellaneous sources	4.6%

2.1.2 Sulfur Dioxide-

Sulfur dioxide is a colourless gas emitted especially from the combustion of coal and oil. SO₂ is emitted into air in some metallurgical roasting and industrial operations also. SO₂ is an extremely corrosive gas. It can react catalytically or photochemically with other pollutants to form sulfur trioxide (rapidly hydrating to sulfuric acid), sulfuric acid and sulfates. Suspended particulate matter and sulfur dioxide are often regarded as the "traditional" pollutants of urban areas. The highest levels of these pollutants occurred during the sulfurous smogs to which most large industrial cities have been subjected in the past. Table 2.2 gives recognised health effects at different concentrations.

Table 2.2
Response To Sulfur Dioxide (Mallette, F.S., 1955)

DESCRIPTION	SO ₂ (ppm)	
LD50, 30 minutes, rat	1800	
Lethal concentration, 113 hrs, guinea pig	112	
Lethal concentration, 30 days at 6 hrs	50	
Mice and Rabbits		
	U*	A*
Man, irritating or objectionable	5-20	10-30
Man, identification	3-12	2-4
Man, detection	2-12	2-3
Man, modified respiratory	1-2	1-10

U*- Unaccustomed to SO₂

A*- Accustomed to SO₂

SO₂ is readily soluble in water and hence it is washed down to earth by rain. Oxides of metals and ash act as catalyst to oxidise SO₂ readily to SO₃ in air. In presence of moisture, SO₃ gives droplets of H₂SO₄, 0.2 to 0.45 micron in diameter. These droplets absorb many organic and inorganic substances from air and form 'smaze' or blue smoke. Smaze is the combined effect of smoke and haze. Smoke results from air borne particles of incomplete combustion, while haze is the condition of diminished visibility due to dust, moisture and salt particles. Sulfur dioxide and sulfur trioxide with moisture and with temperatures (which

encourage formation of fog droplets that readily dissolve SO_2 and SO_3 to produce acids) in the world is reported to be increasing by 0.006 ppm per year (Devitt, et al., 1989). But it is washed down as sulfates when it reacts rapidly with ammonia, calcite, dust, air-borne alkalies etc.

2.1.3 Emission Of Sulfur Dioxide-

All natural oil and coal contains sulfur in varying composition from 0.1 to over 5.0 percent and that depends on nature or the origin of fossil fuel (Work, et al., 1981). In order to meet ambient air quality standards, government has established specific emission standards for a number of industries. Table 2.3 gives the sulfur dioxide content of combustion gases from several typical fuels (Khol, et al., 1979).

Table 2.3
Sulfur Dioxide Concentration In Combustion Flue Gases*
(Khol, et al., 1979)

FUEL	SO_2 IN FLUE GAS (%)
Coal 4% Sulfur	0.35
Fuel oil 2% Sulfur	0.12
Fuel oil 5% Sulfur	0.31
Refinery acid sludge, 40% H_2SO_4	2.0

* Fifteen Percent Excess Air

Coal obtained from mining has a sulfur content of 2.0 to 2.5%. Hence control measures must be instituted on fossil fired combustion processes (Work, et al., 1981). Coal containing sulfur less than 2% are known as low sulfur coal, while high sulfur coal has more than 2% sulfur (Laseke, et al., 1980).

2.2 CONTROL OF SULFUR DIOXIDE

Figure 2.1 gives the categorization of sulfur dioxide removal processes. The technical and economic feasibility of an SO_2 removal process depends on the type and the quantity of effluent gases that must be cleaned. Removing the sulfur from the fuel or removing SO_2 from the exhaust gases are two basic approaches to SO_2 emission control (Miller, 1986; Stern, 1977; Muzio, et al.; 1987, Offen, et al., 1987; and Hunger, et al., 1968).

2.2.1 Sulfur Dioxide Control From Power Plant Flue Gas-

The potential methods to reduce the sulfur dioxide emission from fossil fuel combustion are (Work, et al., 1981)-

- A. Change to low sulfur fuel
 - 1. Natural gas
 - 2. Liquefied natural gas
 - 3. Low sulfur oil
 - 4. Low sulfur coal
- B. Use desulfurized coal and oil
- C. Use flue gas desulfurization (FGD) system
- D. Tall stack emission of SO_2 remaining after FGD (for meeting standards.)

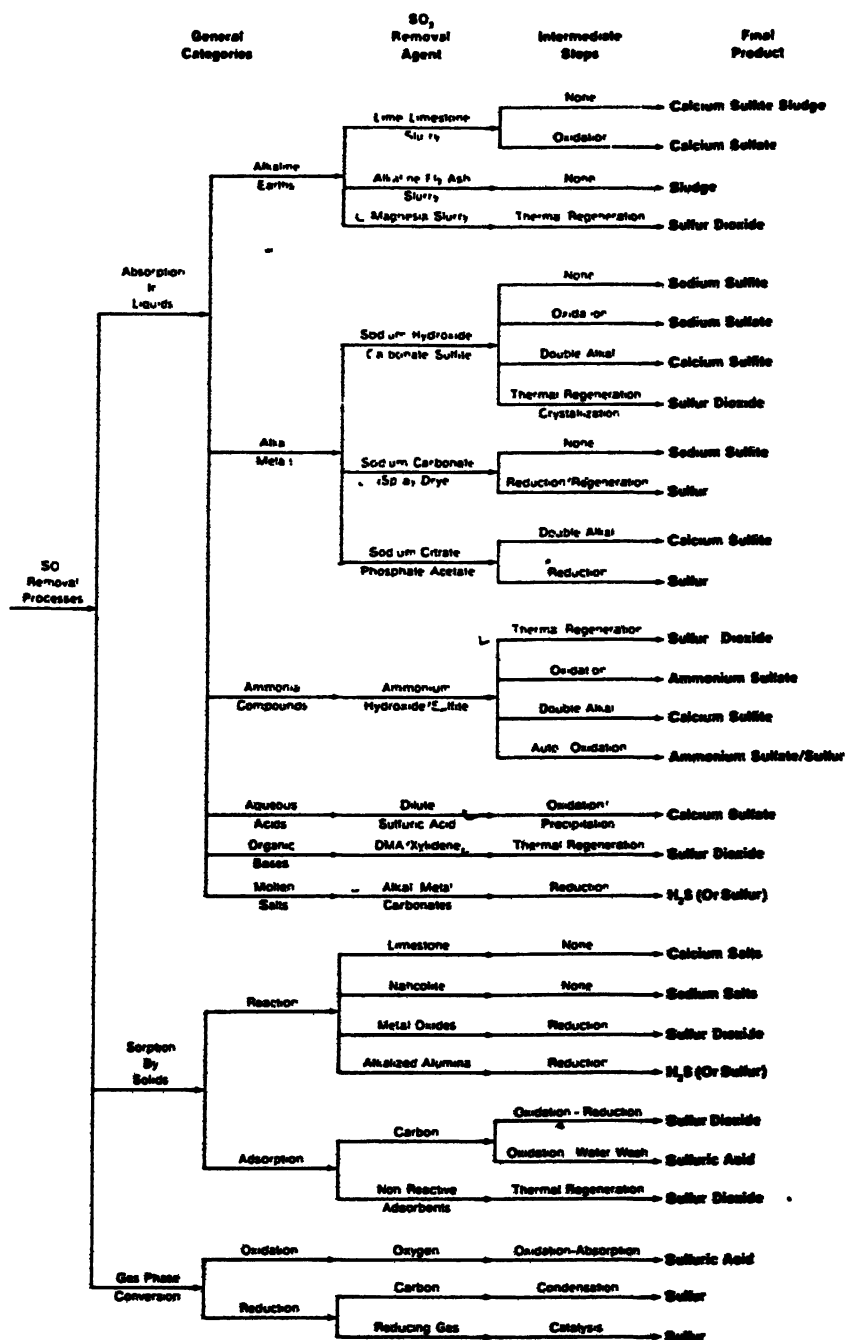


Fig.2.1 Categorization Of Sulfur dioxide removal Processes (Khol, 1979)

Power plant flue gas generally contain low concentration of SO_2 (<0.5 percent by volume), but the volumetric flow rate of emission is found to be quite high, which creates problem during control of SO_2 .

2.2.2 Flue Gas Desulfurization System-

Presently it is the most commonly used technology. The highest level of SO_2 removal is achieved by post combustion control processes (Muizo, et al., 1987).

Flue Gas Desulfurization processes may be grouped according to two classifications:

1. Throwaway or Regenerative
2. Wet or Dry

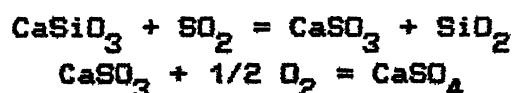
A throwaway process uses cheap base that reacts with sulfur dioxide to form the solid sulfites, which is simply disposed as waste. Regenerable process is either thermal regeneration to recover the acid gas as a concentrated SO_2 stream (sodium sulfite, magnesium oxide) or reaction with H_2S to produce elemental sulfur (citrate and phosphate processes).

In throw away processes, there is a strong economic incentive to use cheapest available base lime or limestone. Sometimes flue gas desulfurization systems use some inorganic salts (eg. NaOH , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ etc.) that enhances the percentage removal of sulfur dioxide. These compounds are known as Deliquescent salt additives. On the otherhand wet or dry processes are differentiated simply by whether the product formed is dry or wet. The removal system

typically involves the use of absorption, adsorption or catalytic processes. In FGD system, the throwaway process is found to be cheapest and less complex than regenerable (Ghosh, et al., 1986).

2.3 SORBENTS FOR DRY SO₂ EMISSION CONTROL

The sorbents indicated to date are primarily either naturally occurring limestone or dolomite or hydrated materials derived from these raw materials and these sorbents have been tested in numerous laboratory tests (Samuel, et al., 1981; Muizo, et al., 1987; Jorgensen, et al., 1987; Jozewicz, et al., 1988; Karlsson, et al., 1983; Chu and Rochelle, 1989; Vijay, 1989; Sandhu, 1990). Limited studies have also been conducted on calcium silicate hot gas desulfurization (Yang and Shen, 1979). It was found that calcium silicate was equally or more reactive than calcium oxide and the regenerative rate of this sorbent was substantially higher than that of calcium oxide. No significant reduction in reactivity was observed even after eight cycles of sorption and regeneration (Yang and Shen, 1979). Calcium silicate undergoes the following reaction.



Thermochemically, CaSO₄ is not stable at temperature above 1250 °C in an environment typical of high sulfur coal-fired combustion products (2000-4000ppm) (Offen, et al., 1987). As sulfation proceeds, CaSO₄ builds up on the CaSiO₃ surface, which requires that the SO₂ diffuse through the CaSO₄ to reach unreacted CaSiO₃. Although the

current understanding of process is still incomplete, it is generally accepted that sulfation can be limited by any of the following processes as the sorbent particles proceeds through the furnace:

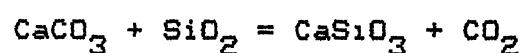
1. Bulk diffusion of SO_2 to the particle
2. Diffusion of SO_2 through pores
3. Diffusion of SO_2 through CaSO_4 layer
4. Filling of small pores, causing a decrease in reactive area
5. Building up of CaSO_4 at the entrance of a pore causing pore closure
6. Loss of surface area due to sintering.
7. Reduced kinetic reaction rates at low temperature.

In actual situation all of the above provide resistance to the sulfation (Muizoz and Offen, 1987). Although, an increased reaction rate between the sorbent and SO_2 is expected from the increased moisture content. Deliquescent or hygroscopic salts as additives have been shown to enhance the performance of the sorbent because of their moisture capturing capacity (Karlsson, et al., 1983).

2.4. WOLLASTONITE-

Wollastonite is a clay mineral found plenty in Rajasthan contains about 99 % CaSiO_3 and appears a potentially useful sorbent for dry SO_2 emission control. Wollastonite is a common constituent of thermally metamorphosed impure lime stone, and may also occur in the invading igneous rock due to contamination. Although normally consisting of fairly pure CaSiO_3 the wollastonite structure can

accept considerable amount of Fe and Mn and lesser amount of Mg to replace Ca. The wollastonite may be formed by the following reaction (Deer, et al., 1963).



The chemical characteristics of wollastonite available in Rajasthan is given below (Sharma, et al. 1988).

SiO ₂	48.5%
CaO	48.48%
Fe ₂ O ₃	0.26%
Al ₂ O ₃	0.24%
Loss on ignition	2.5%
Mean particle diameter	40 micron
Surface area	1.18 sq.m/gm
Porosity	0.23
Density	2.21 gm/cu.cm

2.5 WASTE DISPOSAL AND UTILIZATION

From the safety hazard point of view, the following issues need to be addressed when designing the waste handling system:

1. Permitting and availability of disposal sites for the new wastes.
2. Fugitive emissions and dust control.
3. Worker protection when handling highly alkaline materials.
4. Tendency to undergo pozzolonic reactions with the fly ash and "set-up" if wet, resulting in a need to avoid any wet/dry interfaces in the waste handling system.

High volume utility wastes, such as ash and FGD sludges, are currently exempted from classification as hazardous under the Resource Conservation and Reclamation Act (RCRA) (Eklund, et al., 1986). Developers have attempted to (1) process the waste for easier disposal by taking advantage of its pozzolonic nature, and (2) utilize the waste as an alternative to disposal. According to the later point the waste from calcium-based dry SO_2 processes may be used as:

- * Stabilizers of wet FGD sludge
- * Feed material to a wet FGD system
- * Construction filler material for road beds and building, i.e. continuation of fly ash utilization practice
- * Feedstock in the production of cement, synthetic or lightweight aggregates or bricks
- * Mineral wool

The cost and potential regulatory limit for disposal of these wastes provide motivation for significant R&D effort to render the wastes harmless and utilizable

Overviewing the review in this section, it can be found that the use of fixed bed reactors, especially if coupled with regenerable sorbent, has a good potential for removing sulfur dioxide from flue gases at very low cost. For Indian conditions where the sulfur content of coal is around 1%, the dry processes of SO_2 removal may be one of the preferred methods. However, before such a FGD system could be dused in field or under pilot plant a detailed study of the process in laboratory is essential.

3. SCOPE AND OBJECTIVE OF PRESENT WORK

The dry sulfur dioxide control systems using solid reactants are less complex and are possibly more flexible with respect to operating conditions. Although conventional wet scrubbers for sulfur dioxide emission control give quite high efficiency, their use is limited because of high capital and operating costs and complexity in the operation of system. A number of dry sulfur dioxide removal processes have been developed by several researchers and are still being developed.

An attempt has been made to study the usefulness of such a process in a laboratory scale set-up for sulfur dioxide removal in a packed bed reactor at various operating conditions using calcium silicate as sorbent. The idea behind using calcium silicate is keeping in view the possible use of the rock wollastonite, which contains about 99% CaSiO_3 . A discussion on wollastonite has been included in section 2.4. The experimental programs have been designed to achieve the following objectives:

1. Studying the effect of inlet SO_2 concentration on SO_2 removal in packed bed.
2. Generation of breakthrough curves for SO_2 in packed beds and to evaluate the kinetic parameters for $\text{CaSiO}_3/\text{SO}_2$ reaction.
3. Studying the effect of humidity of test gas on SO_2 removal.

4. Finally extending the above program to obtain empirical equations for SO_2 removal at different operating conditions (within the range studied).

It may be mentioned that the present investigation mainly focuses on the sulfation reaction in the low temperature range (100 - 240 °C). It is expected that this experimental study will throw light on the extent of utilization of solid sorbent under the various process conditions stated above.

4. EXPERIMENTAL SETUP AND OTHER FEATURES

4.1 EXPERIMENTAL SETUP

The experimental setup used for conducting the experiment has been shown in Fig.4.1. A packed bed system was used to study the performance of reactor under different conditions of average temperature, relative humidity, and inlet sulfur dioxide concentration etc. The packed bed system consisted of reactor of vertical tube of glass 27mm ID and 60cm in length. The lower section of reactor was made as preheater, while the upper section served as the reactor packed with solid sorbent upto desired height.

4.1.1 PREPARATION OF TEST GAS

In the present work the mixture of sulfur dioxide and air was used as test gas. Sulfur dioxide was taken from the commercially available SO_2 gas cylinder, while the air was taken from an air pump (compr-1 essorac-70, manufactured by scientific instrument Co. Ltd., N. Delhi). The flow was measured with the help of manometer assembly, however, it was controlled with the help of needle valve. To mix properly, a glass tube (about 25 mm ID and 20 cm long) was used, which was packed with glass beads and glass wools. The two gases were let to the bottom of the tube and come out of it from top after mixing.

A rotometer of 6.6 liter per minute capacity was used to monitor the flow rate of the test gas. A glass flask filled with

T_o = Inlet Temperature probe
 T = Outlet Temperature probe
 S = Test Gas Sampling points

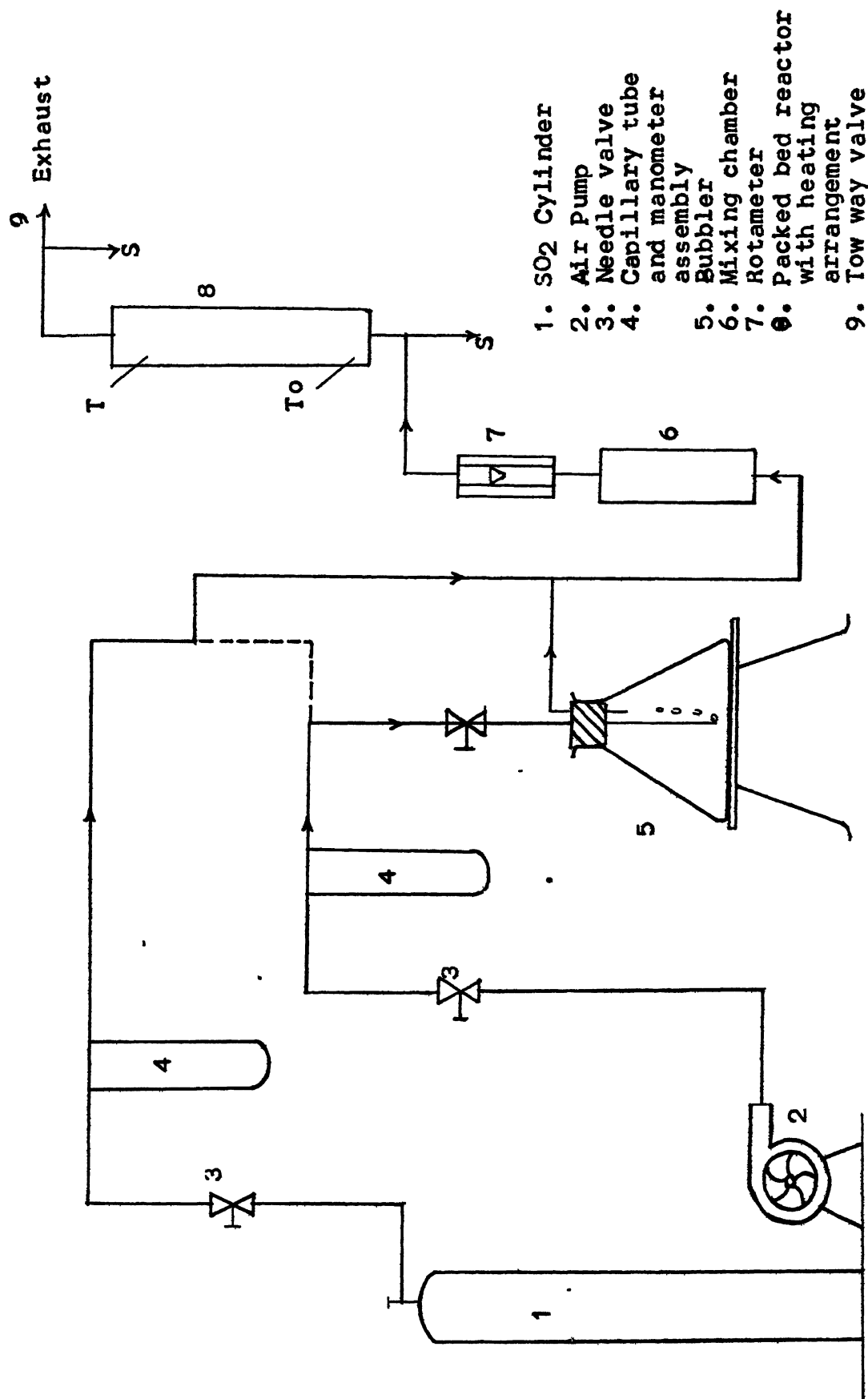


Fig.4.1 Experimental Set-Up

water was used to vary the humidity of test gas. For this, the air was bubbled through it and then mixed with SO_2 . Relative humidity was measured by noting down the dry and wet bulb temperature and using psychometric chart.

4.1.2 REACTOR SYSTEM

The reactor itself was used as heating system. It was a glass tube of 27 mm diameter and 60 cm long. The heating arrangement was made with the help of heating coil wrapped along the glass tube. An insulation of 10 mm thick glass wool was provided. The temperature of the test gas was regulated by controlled heat input by controlling the current through the heating coil.

In the reactor the sand bed mixed with solid sorbent was provided with some glass wool over it. It had two port holes, one at the top and another at the bottom of the sand bed for the measurement of temperature at these points.

4.1.3 SAMPLING POINTS

An impinger and aspirator bottle arrangement was used for sampling of the test gas to measure the inlet and outlet concentration as shown in Fig.4.1, that is just before the reactor. The effluent gas was allowed to cool down before it was sampled.

4.2 TESTING FEATURES

Table 4.1

Details Of Sand Bed

Type of sand	: Ganga river sand
Average sand size:	0.456 mm
Bulk density	: 1.463 gm/cu.cm
Porosity	: 46%
Bed Diameter	: 27 mm
Height of bed	: 11.2 cm

Table 4.2

OPERATING CONDITIONS

Test gas composition	: SO ₂ in air
Concentration of SO ₂ in test gas	: 500-1500 ppm
Temperature of test gas	: 100-240 deg.C
Flow rate	: 2.0 lpm
Space velocity	: 1876/hr
Residence time of test gas in sand bed	: 1.92 sec.

5. MATERIAL AND METHODOLOGY

5.1 MATERIALS

All glassware were made of 'pyrex' glass manufactured by Borosil Glass Works Ltd. Bombay and marketed under the branch name 'Corning'. All chemicals used for preparation of reagents, for estimation of sulfur dioxide concentration were of analytical reagent grade. Water used during whole experiment, in the preparation of reagents and all other experimental work was sulfate free laboratory distilled water.

5.1.1 *SORBENT BED*

For the preparation of sorbent bed the local sand (Ganga river sand) was passed through 500 micron sieve and retained at 425 micron sieve (thereby giving average size 0.456 mm) (Gupta,S.K.,1982) was used. The sand was first washed with tap water and finally with distilled water to sort out the impurities and then it was dried at 105 °C for 24 hours.

As suggested by other researchers (Jorgensen,et al.,1987; Jozwiez,et al.,1988 and Karlson,et.al.1983) one gram Calcium silicate was dispersed in 50 gram of sand to make sorbent bed, this proportion gives a good dispersion of sorbent in sand. Calcium silicate was mixed in sand by dry procedure. A thorough

mixing was done to make a uniform dispersion.

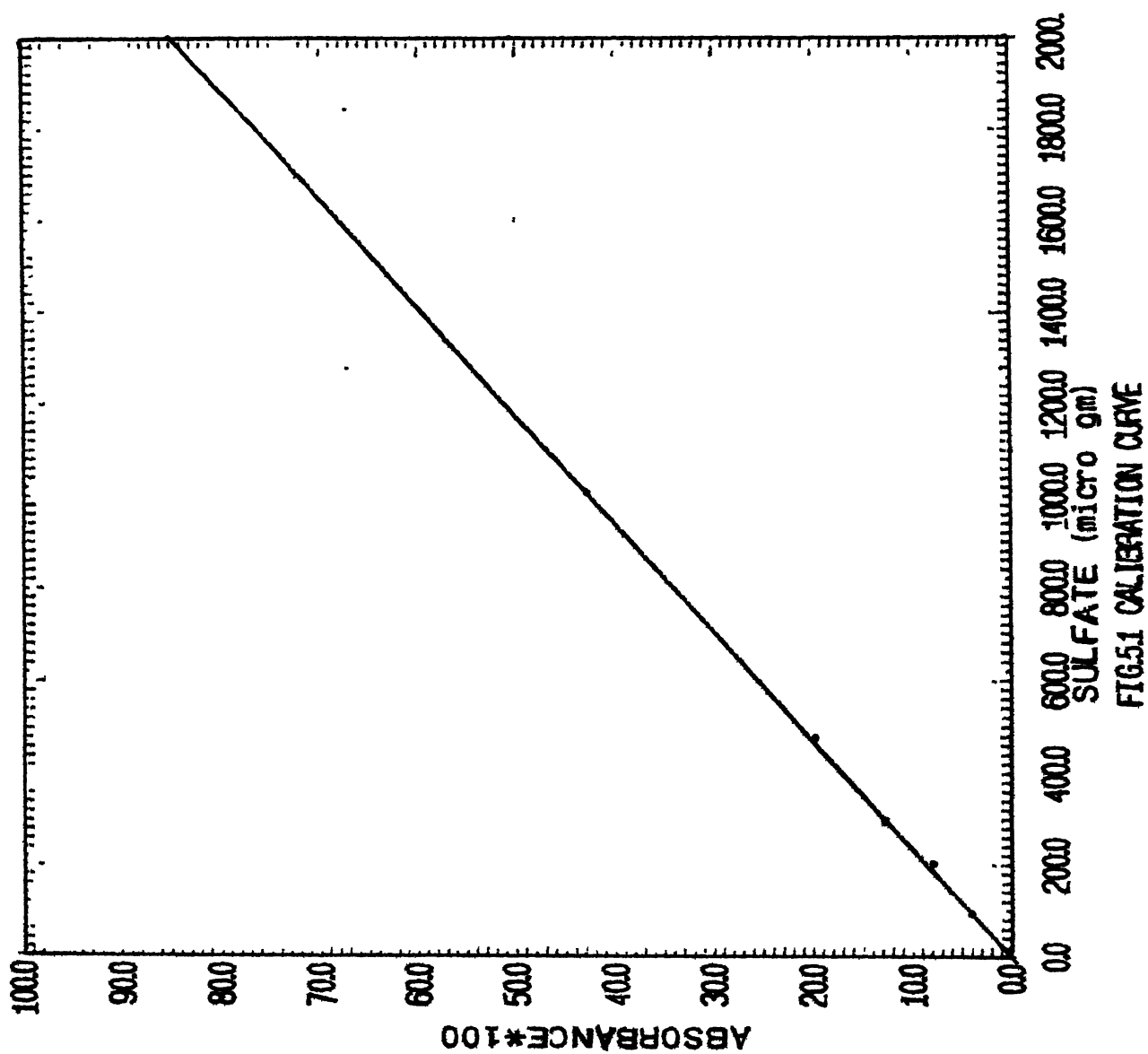
5.1.2 TEST GAS

The test gas used in all the experiments consisted of sulfur dioxide gas from commercially available SO_2 gas cylinder, with air as dilutant. The desired concentration level of sulfur dioxide in the test gas mixture was maintained by individual and accurate control of flow of air and sulfur dioxide gas. The two gas streams were mixed in a mixing chamber to ensure a uniform composition of gas mixture. The humidity of gas could not be varied too much because of unavailability of instruments. So experiments were conducted at about 41% humidity.

5.2 METHODOLOGY

5.2.1 ANALYTICAL TECHNIQUE USED FOR SULFUR DIOXIDE ESTIMATION

In the present work the sulfur dioxide concentration in the test gas was measured by 'Barium Sulfate Turbidity Method'. In this method the SO_2 from the test gas was absorbed in absorbing solution (30% H_2O_2 solution). Barium chloride is used to form Barium sulfate. The principle behind this is, the sulfate ion reacts with barium ion to form insoluble barium sulfate. A colloid stabilizing agent is added to stabilize the suspension of BaSO_4 . The absorbance of the sample at 500 nm is read before and after the addition of BaCl_2 to compensate for any coloration or turbidity present in the sample. A calibration curve was plotted (Fig 5.1)



for differential absorbance against micro gram sulfate. However, differential absorbance was measured with the help of Spectrophotometer- 106 (Systronics Pvt. Ltd., New Delhi). Thus by measuring the amount of sulfate present in absorbing solution, the concentration of sulfur dioxide in test was calculated by the method given in Appendix-A.

A standard plot (Calibration curve) for SO_2 concentration estimation was prepared using standard sulfate solution. The plot has been shown in Fig.5.1. For higher concentration of sulfur dioxide in test gas mixture sampled, dilutions were made before analysis.

NOTE: This method was used because of unavailability of some chemicals. Although this method has the poorest sensitivity, precision and accuracy at low levels, ~~but~~ in our case the concentration is in the of hundreds of ppm, so the results obtained expected to be correct. For sulfate concentration between 15 and 100 micro gm/ml (range studied 33-98 micro gm sulfate/ml), the coefficient of variation ranges from 0.7 to 8.4%, typically about 3.5%. Accuracy within this range is within $\pm 6.3\%$. (James, et al., 1989).

5.2.2 EXPERIMENTAL TECHNIQUE

In the present work, the packed bed reactor was used and a series of experiments were performed to test the reactivity of

sorbent with sulfur dioxide.

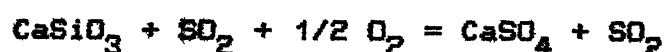
Sorbent used in present work was calcium silicate. The three main variables expected to influence the reactivity of sorbent were identified as sulfur dioxide concentration in the test gas, average temperature and relative humidity.

During the test it was made sure that the gas concentration in test gas mixture and the temperature at the inlet are reasonably constant. The gas mixture was passed through sand bed and samples at inlet and outlet were taken at regular time intervals. For each sampling the gas was passed for 10 seconds through 20 ml of absorbing solution with the help of impinger and aspirator bottle arrangement. The samples were collected and analyzed by 'Barium Sulfate Turbidity Method'. All the measurements were taken at room temperature.

5.2.3 ORDER OF REACTION AND REACTION RATE CONSTANT

For the present study the plug flow model for the reactor is found to be a reasonable assumption (Appendix-D). For plug flow reactor mode, the performance equation is (Levenspiel, 1972)

$$\tau = \frac{V_0}{V_0} = C_{SO_2}^0 \int_0^{x_f} \frac{dx_{SO_2}}{-r_{SO_2}} \quad \dots\dots\dots 5.3.a$$



where,

ϵ = Porosity of the bed

τ = Space time, hr

V = Bed Volume, m^3

V_0 = Gas flow rate, m^3/sec

$-r$ = Rate of disappearance of SO_2 (mole/ m^3)/sec.

For n^{th} order reaction, the reaction rate is expressed as-

$$-r = -\frac{dN_{SO_2}}{dt} = k C_{CaSiO_3} C_{SO_2}^n$$

as $C_{CaSiO_3} \cong C_{CaSiO_3}^0$ and $C_{SO_2} = C_{SO_2}^0 (1 - X_{SO_2})$

and $C_{CaSiO_3}^0 = \frac{N_{CaSiO_3}^0}{V(1-\phi)}$

or
$$-r = \frac{k N_{CaSiO_3}^0}{V(1-\phi)} C_{SO_2}^n (1 - X_{SO_2})^n \quad \dots\dots 5.3.b$$

where,

$C_{SO_2}^0$ = Inlet SO_2 concentration (mole/ m^3)

C_{SO_2} = SO_2 concentration at any time t (mole/ m^3)

X_{SO_2} = SO_2 removal at any time t , fraction

X_{fSO_2} = final SO_2 removal, fraction

$N_{CaSiO_3}^0$ = Sorbent used (moles)

k = Rate constant for reaction (m^3/mol) n /sec

n = Order of reaction

$$\tau = -\frac{V_0}{V_0} = C_{SO_2}^0 \int_0^{X_{SO_2}} \frac{dX_{SO_2}}{-r_{SO_2}}$$

or
$$-\frac{V_0}{V_0} = C_{SO_2}^0 \int_0^{X_{fSO_2}} \frac{V(1-\phi) dX_{SO_2}}{k N_{CaSiO_3}^0 C_{SO_2}^n (1 - X_{SO_2})^n}$$

On solving the above equation

$$1 - (1 - X_{fSO_2})^{1-n} = \frac{C_{SO_2}^0 n^{-1} (1-n)}{V_0 (1-\phi)} k N_{CaSiO_3}^0 \quad \text{for } n \neq 1 \quad \dots 5.3.c$$

for $n=1$

$$\frac{V_0}{V} = C_{SO_2}^0 \int_0^{X_{SO_2}} \frac{V(1-\phi) dX_{SO_2}}{k N_{CaSiO_3}^0 C_{SO_2}^0 (1-X_{SO_2})}$$

On solving the above equation

$$-\ln(1 - X_{SO_2}) = \frac{k N_{CaSiO_3}^0}{V(1-\phi) V_0} \quad \text{for } n=1 \quad \dots 5.3.d$$

All symbols have same meaning as explained earlier. Now we have to fit the straight line $y=mx$ $m^0, (x^0), (y^0)$

(Kreyszig, 1989)

$$\sum (Y^0 - mX^0)^2 = S$$

$$\sum (Y^{02} + m^2 X^{02} - 2mX^0 Y^0) = S$$

$$\sum Y^{02} + m^2 \sum X^{02} - 2m \sum X^0 Y^0 = S$$

$$\partial S / \partial m = 0 + 2m \sum X^{02} - 2 \sum X^0 Y^0 = 0$$

$$\text{or } m_{av} = \frac{\sum X^0 Y^0}{\sum X^{02}} \quad \text{and } m_1 = -\frac{Y_1}{X_1} \quad \dots 5.3.e$$

$$\text{Unit of } k = (m^3/\text{mole})^n / \text{sec.}$$

$$\text{Fractional deviation in Rate constant value} = \frac{\sum (k_{av} - k_i)^2}{\sum k_{av}^2} \quad \dots 5.3.f$$

From the equations 5.3 the fractional value for different orders can be found. The actual order of reaction will be that gives minimum fractional deviation and corresponding rate constant will be the actual rate constant.

6. RESULTS AND DISCUSSION

The experimental data, calculated results, the effect of variables on percent SO_2 removal and SO_2 breakthrough curves in packed bed are shown in tables and figures in this section.

6.1 EFFECT OF INLET SO_2 CONCENTRATION ON SO_2 REMOVAL

Experiments were conducted in a packed bed of solid sorbent with inlet SO_2 concentration between 500 and 1500ppm which is the range of SO_2 emission for most of coals used in field applications (Offen. et. al., 1987). The space velocity was kept at 1876/hr (Residence time = 1.91sec. i.e. near about 2.0 sec. which is usually provided for such gas solid reactors), and that of temperature was kept at 120 °C. For two different relative humidity of test gases, Fig.6.1 and Fig.6.2 show the fractional outlet/inlet concentration of SO_2 (C/C_0) vs. time for three different inlet concentrations of sulfur dioxide. However, a better comparison of both above figures is shown in Fig.6.3. The percent removal of SO_2 and percent utilization of Calcium Silicate, for both the cases at various concentration were calculated have been reported in Table 6.1. The calculation of these values, for a typical breakthrough curve at inlet SO_2 concentration of 1000ppm is shown in Appendix-C. It is very clear from both these figures that, with increase in the

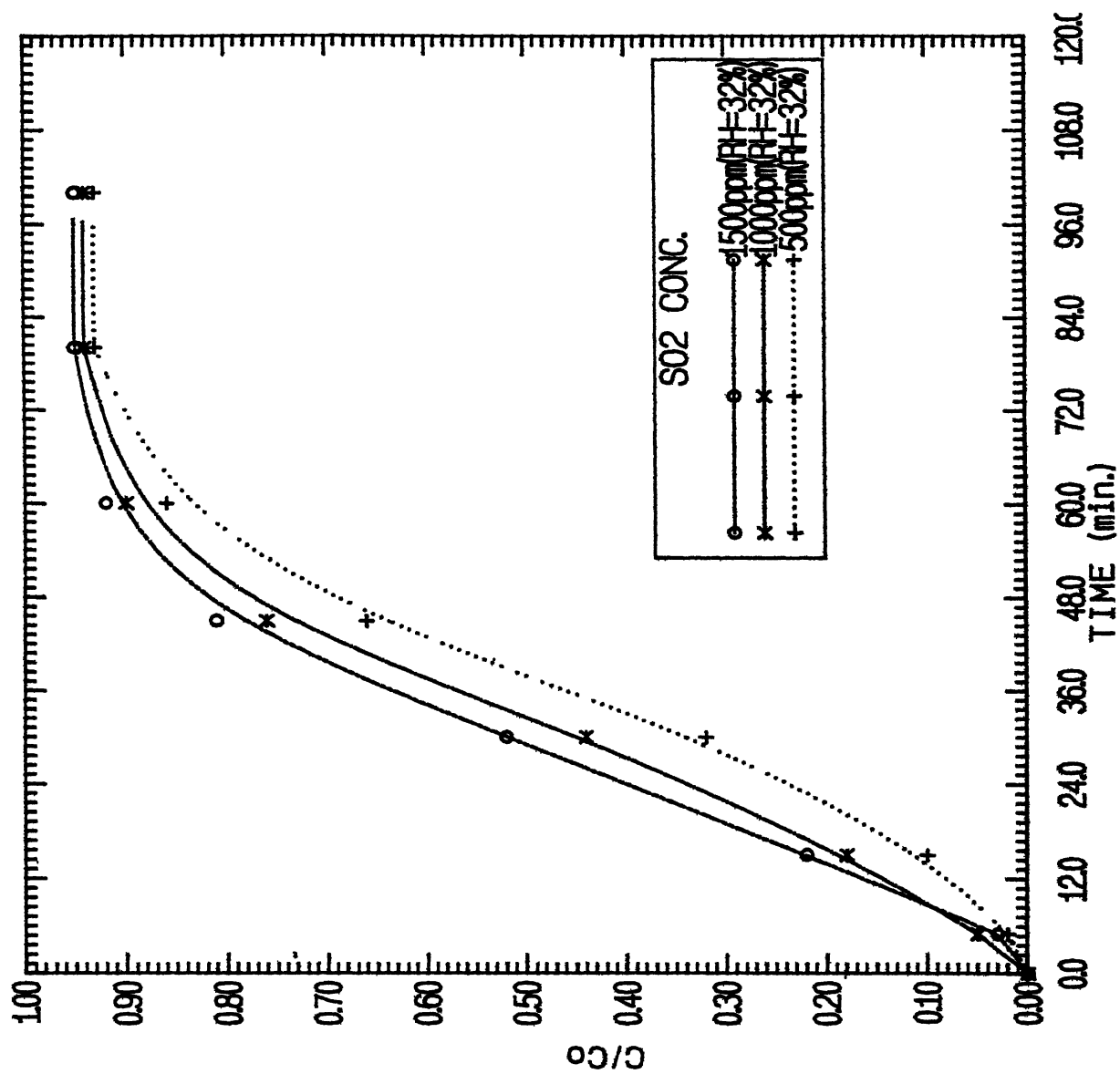


FIG.6.1 EFFECT OF INLET SO₂ CONC. ON SO₂ REMOVAL USING CaSiO₃
SORBENT IN SAND BED (TEMP.=120deg.C, SPACE VEL.=1876/hr, RH=32%)

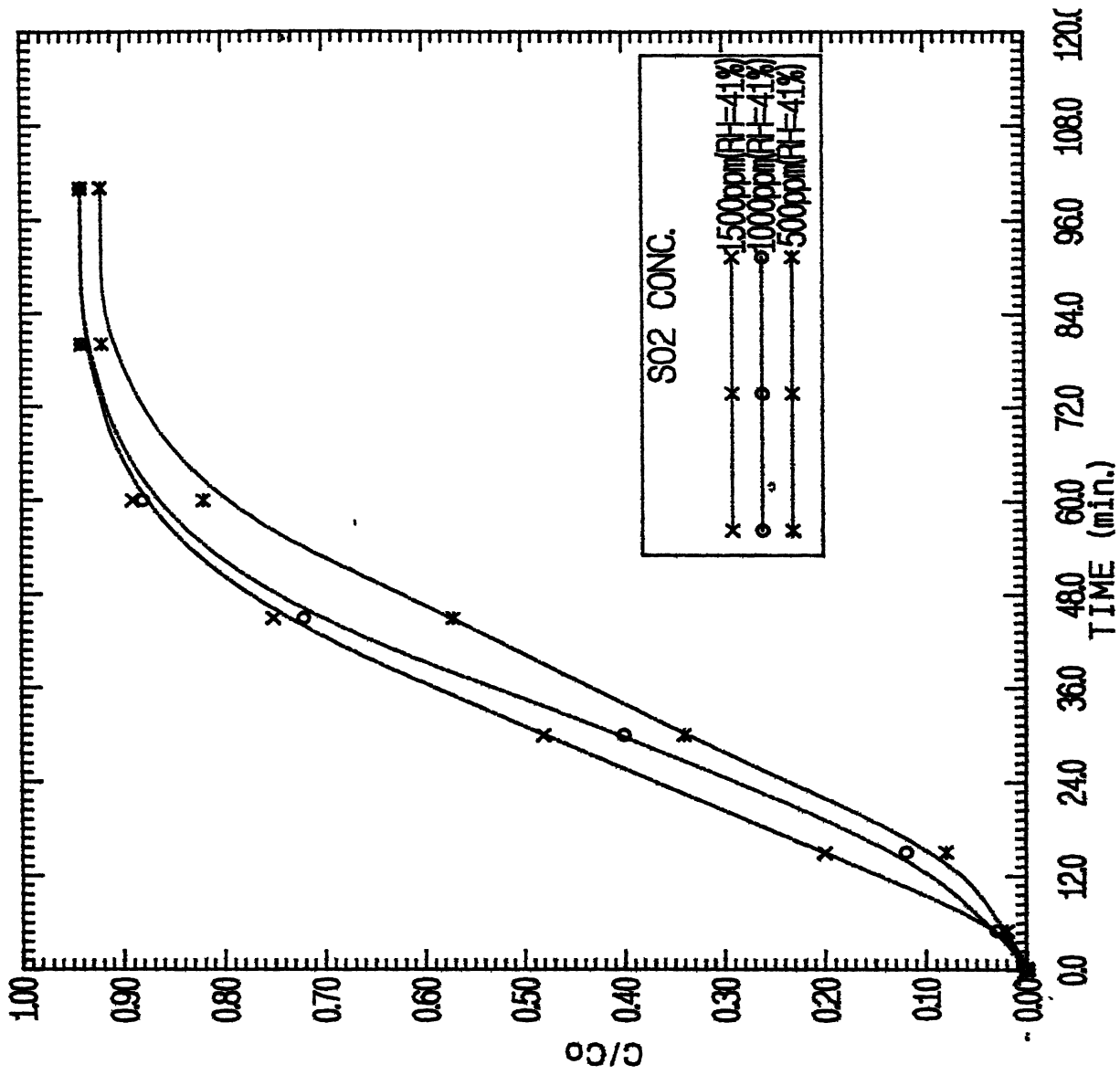


FIG.6.2 EFFECT OF INLET SO₂ CONC. ON SO₂ REMOVAL USING CaSiO₃ SORBENT IN SAND BED (TEMP.=120deg.C, SPACE VEL.=1876/hr, RH=41%)

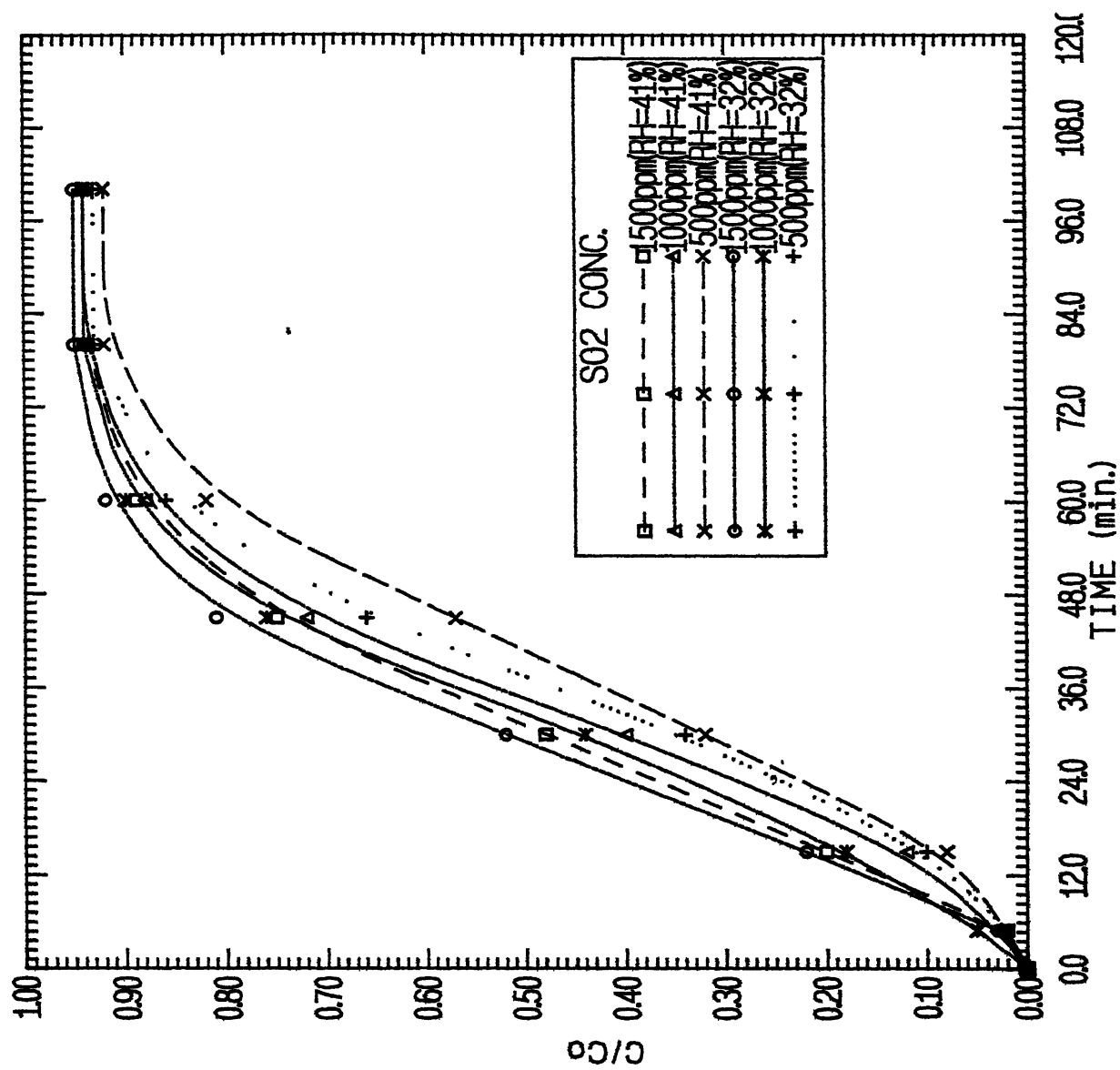


FIG.6.3 EFFECT OF INLET SO₂ CONC. WITH RH ON SO₂ REMOVAL USING
CaSiO₃ SORBENT IN SAND BED (TEMP.=120degC, SPACE VEL.=1876/hr)

inlet sulfur dioxide concentration, the initial break through of sulfur dioxide occurred quicker. Table 6.1 indicates that with increase in inlet concentration of sulfur dioxide the percent utilization of sorbent increases. The overall rate of conversion of SO_2 with sorbent depends on the following (Jorgensen, et al., 1987).

1. Diffusion of gaseous SO_2 to the surface of the solid particle.
2. Penetration and diffusion of SO_2 through the ash layer to the surface of the unreacted core.
3. Reaction of SO_2 with sorbent at the core reaction surface.

As the inlet SO_2 concentration increases, the partial pressure of gas increases, which makes it possible to penetrate and diffuse the gas through the product layer to the unreacted core and thus increases the percent utilization of sorbent. Table 6.1 also shows the changes due to change in relative humidity. The percent increase in sorbent utilization is more or less the same as the percent change in SO_2 removal for a particular inlet SO_2 concentration.

Table 6.1Effect of Inlet SO₂ Concentration on SO₂ Removal Using CaSiO₃Sorbent

Temperature of Test Gas = 120 °C

Space velocity = 1876/hr

Inlet SO2	TEST GAS WITH RH = 32%	TEST GAS WITH RH = 41%	PERCENT CHANGE	μm
conc.	Percent	Percent	Percent	Percent
ppm	Utilization	Removal	Utilization	Removal
	of CaSiO ₃	of SO ₂	of CaSiO ₃	of SO ₂
500	8.05	42.44	8.84	46.56
1000	13.90	36.62	15.09	39.75
1500	19.29	33.88	21.17	37.18

6.2 ORDER OF SULFATION REACTION

A set of SO₂ breakthrough curves has been shown in Fig.6.4 with the various quantities of the sorbent in the packed bed. It can be observed that the SO₂ removal is increasing with increasing quantity of sorbent, which is quite obvious. Fractional removal of SO₂ were calculated for various quantities of sorbent (as indicated in Appendix-C) have been shown in Table 6.2. The order of reaction was expected to be near about one, as reported in literature (Jorgensen, et al., 1987). In order to have an idea about the accuracy of our experimental data it is

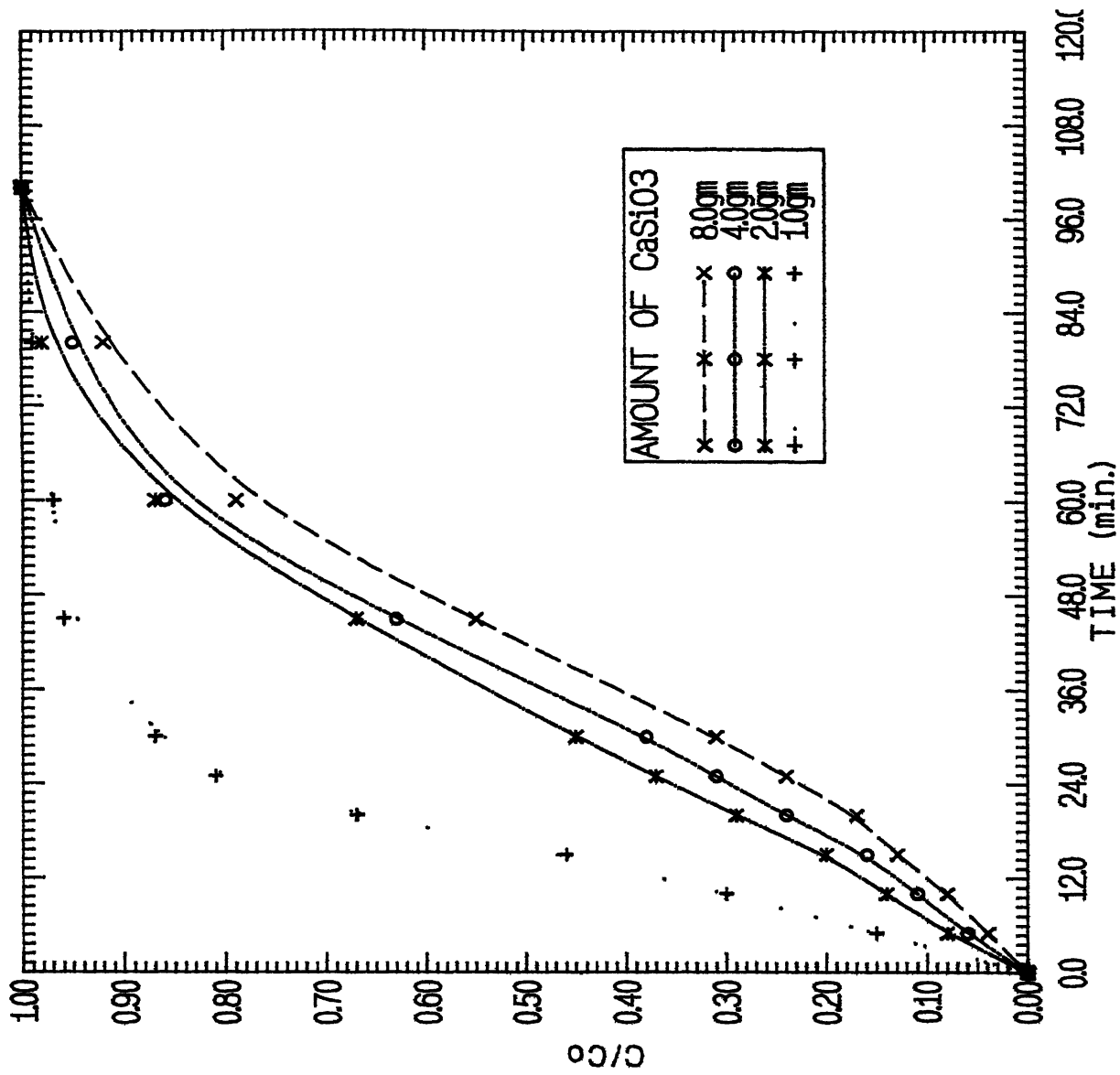


FIG.6.4 EFFECT OF CaSiO₃ CONC. IN SAND BED ON SO₂ REMOVAL
 (TEMP.=120deg.C,SPACE VEL.=1876/hr,RH=41%,C₀=1000ppm)

worthwhile to calculate the order of reaction. The method used for finding the order of reaction consists of selecting different values for the order of reaction and calculating the corresponding value of rate constant. The value of order of reaction which minimizes the variation in k is the desired value of order of reaction (Levenspiel, 1972). The minimization was done using method of least squares (Kreyszig, 1989) for fractional deviation calculation.

The order of reaction which minimizes the variation in the value of rate constant was found to be 1.1 with the help of equations 5.3, which is close to 1.0 within experimental limits. It would have been really surprising to get the order of reaction exactly equal to 1.0 because that would amount to a perfect experiment! A fortran program was written (Appendix-E) for equations 5.3 and the results obtained are shown in Table 6.2. Fig. 6.5 has been plotted on the data given in Table 6.2. For all the calculations in other sections the order of reaction was taken as 1.0.

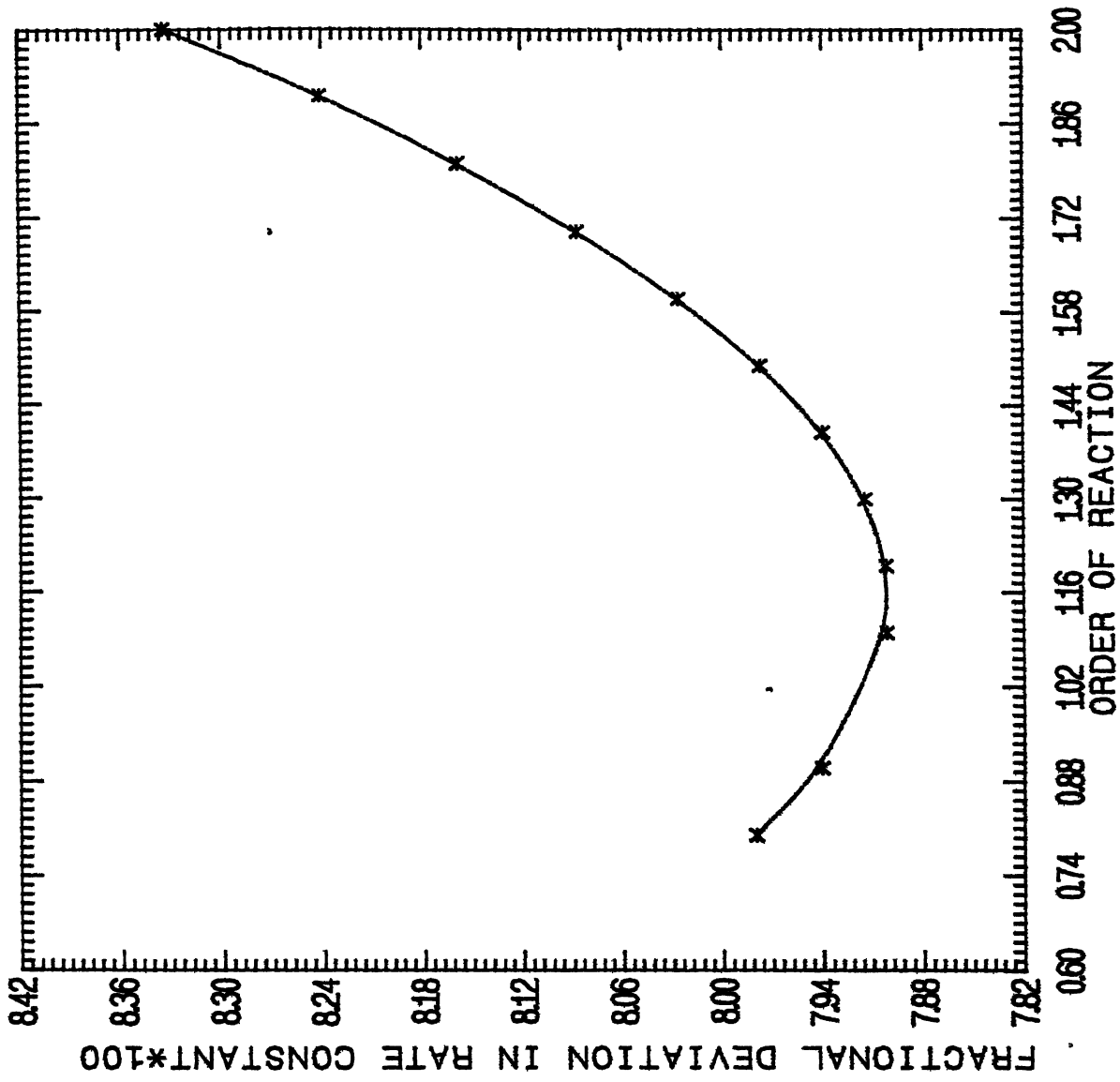


FIG.6.5 ORDER OF REACTION VS FRACTIONAL DEVIATION IN RATE CONSTANT
VALUE FOR $\text{CaSiO}_3/\text{SiO}_2$ REACTION

Table 6.2

Variation Of Fractional Deviation And Rate Constant With Order Of Reaction

Sorbent Quantity (mmol)	Fractional Removal Of SO ₂ (x)	(1-x)
8.62	0.144	0.856
17.24	0.386	0.614
25.86	0.396	0.604
34.48	0.412	0.588

Order Of Reaction (n)	Percent Fractional Deviation	Rate Constant ³ ((m/mol)**n)/sec.
0.8	7.98	3.61865E-04
0.9	7.9405	5.10642E-04
1.0	7.9022	7.39324E-04
1.1	7.9017	1.01753E-03
1.2	7.9018	1.43684E-03
1.3	7.9145	2.02940E-03
1.4	7.9397	2.86698E-03
1.5	7.9769	4.05115E-03
1.6	8.026	5.72572E-03

6.3.1 EFFECT OF BED TEMPERATURE ON SO₂ REMOVAL

The effect of temperature on SO₂ removal in the temperature range 100-240 °C (usual temperature range of flue gas, downstream of economizer 120-203 °C) with calcium silicate as sorbent is shown in Fig.6.6. It can be seen from Fig.6.6, as the

temperature increases, the removal of SO_2 also increases resulting in delaying of SO_2 breakthrough. Conversion (mol SO_2 /mol CaSiO_3), percent removal of SO_2 and percent utilization of CaSiO_3 have been shown in Table 6.3 (Calculated as in Appendix-C). Fig.6.6 shows that breaking through is quicker at lower temperature (viz. at 100°C). This may be due to the fact that sulfation reaction is faster at higher temperature leading to better utilization of CaSiO_3 which is also evident from Table 6.3.

Table 6.3

Effect Of Temperature On SO_2 Removal In Packed Bed

Inlet SO_2 concentration: 1000ppm

Sorbent : 2 gm CaSiO_3 dispersed in sand

Space velocity : 1876/hr

Relative Humidity : 41%

Temperature ($^\circ\text{C}$)	Conversion mol SO_2 /mol CaSiO_3	Percent Utilization of CaSiO_3	Percent SO_2 Removal
100	0.1429	14.29	37.66
150	0.1465	14.65	38.61
200	0.1494	14.94	39.37
240	0.1530	15.30	40.31

6.3.2 REACTION RATE CONSTANT, ACTIVATION ENERGY AND FREQUENCY FACTOR

From the breakthrough curves (Fig.6.6) at different temperatures the removal of SO_2 was calculated (as indicated in Appendix-C). With the help of equation 5.3.d the rate constants have been calculated which are shown in Table 6.5. It can be seen very clear from the table that as the temperature increases, the removal of SO_2 as well as the rate constant increases.

According to Arrhenius' law the temperature dependency of rate constant is as follows (Levenspiel,1972):

$$k = k_0 e^{(-E/RT)} \dots\dots\dots 6.3.a$$

where,

k = Reaction rate constant

k_0 = Frequency factor

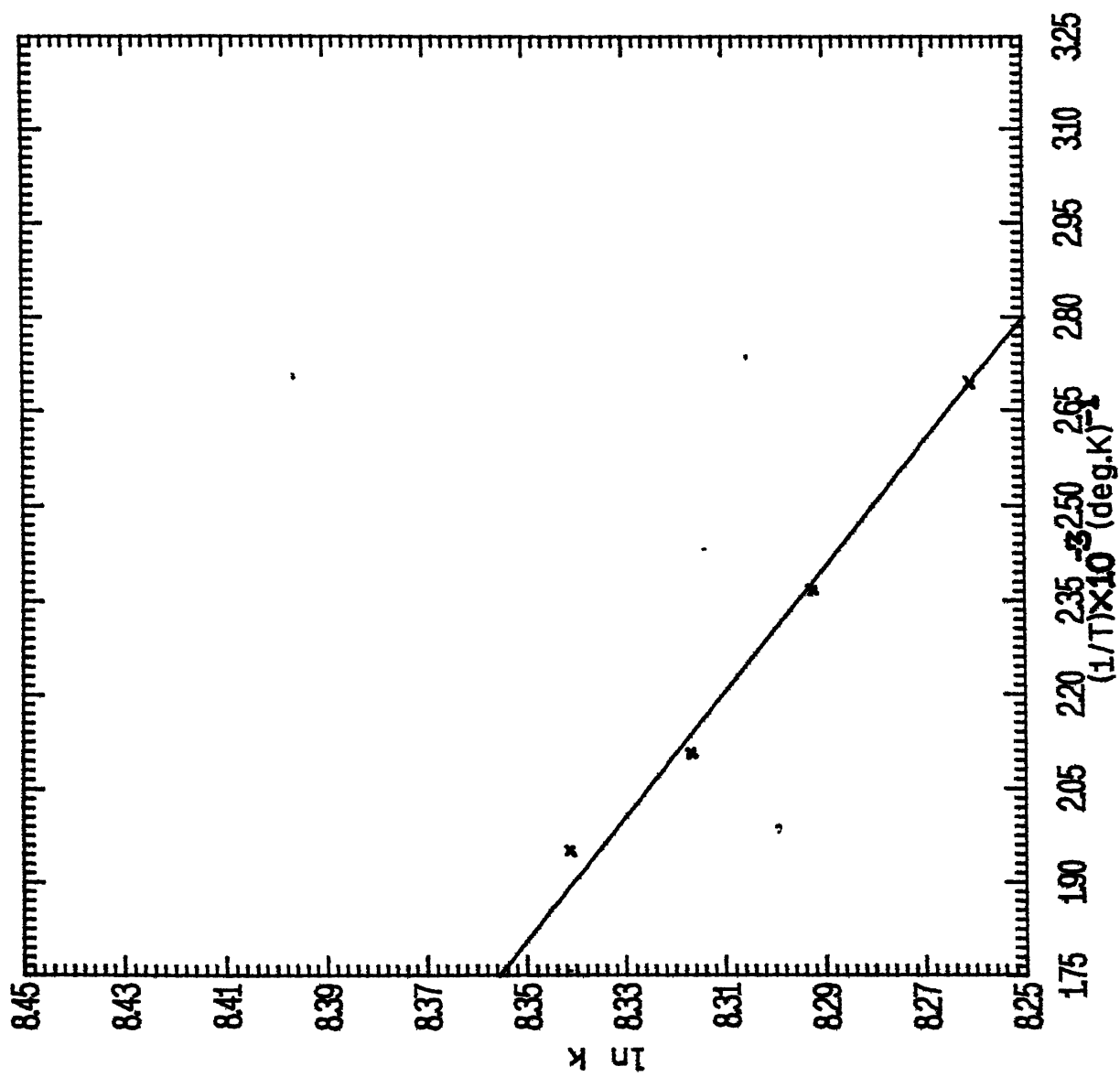
E = Activation energy of reaction

R = universal gas constant

An Arrhenius plot has been shown ($\ln k$ vs. $1/T$) in Fig.6.7 and the slope of the plot was found to be -99.52 i.e.

$$-E/R = -99.52$$

Activation Energy, $E = 199.04 \text{ cal}$
& Frequency Factor, $k_0 = 5614.77$

FIG.6.7 TYPICAL ARRHENIUS PLOT FOR CALCIUM SILICATE-SO₂ SYSTEM

and the temperature dependency of reaction rate constant (in the temperature range studied) can be depicted as†

$$k = 5614.77 e^{(-199.04/RT)}$$

Where,

T = Temperature, °K

R = Universal Gas constant, cal/°K/mol

k = Reaction Rate Constant, (l/mol)/hr

Table 6.4
Reaction Rate Constants

Temperature °C	Fractional SO ₂ Removal	Rate Constant (l/mol)/hr
100	0.3766	3861
150	0.3861	3987
200	0.3937	4081
240	0.4031	4216

6.4 EFFECT OF RELATIVE HUMIDITY ON SO₂ REMOVAL

The humidity in test gas was maintained by bubbling the air through water. The relative humidity of test gas was obtained using psychrometric charts by observing dry bulb and wet bulb temperatures of test gas. The relative humidity of test gas could not be maintained to the desired extent because of unavailability of instruments. Fig.6.3 shows the effect of humidity, present in the

test gas on SO_2 removal. Table 6.1 shows the percent utilization of sorbent and percent SO_2 removal (calculated as in Appendix-C), in 80 minutes run at 120°C and at relative humidities 32% and 41%. It was found that breakthrough of SO_2 occurred earlier at lower relative humidity. The percent utilization and percent SO_2 removal increase as the humidity increases. The results can be explained on the basis of diffusion resistance. The reduction in resistance may occur due to water adsorption on the particle (Jorgensen, et al., 1987).

It may be mentioned that X-ray diffraction of the reacted sorbent indicated the presence of calcium sulfate. The reaction product, CaSO_4 formed was reported to be too dense and impermeable for the further diffusion of the reacting gaseous species into the unreacted inner sorbent core (Keener, et al., 1984).

6.5 EMPIRICAL EQUATIONS FOR SO_2 REMOVAL AT DIFFERENT OPERATING CONDITIONS

The above experimental program was extended to find out the general empirical equations at various operating conditions using numerical analysis and the data obtained from experiment. The equations thus obtained are useful to get fractional removal of SO_2 at any operating conditions within the range studied. For this, at a particular operating condition the variation of C/C_0 with time was studied with the help of graphs to see whether it followed square, cubic or 4^{th} power polynomial. Then with the help of a computer program (Davidon Fletcher Powell Method) for that type of spline, the equation was found.

For example in the case of inlet SO_2 concentration variation, three sets of data 1500, 1000 and 4500 ppm will give three equation

in C/C_o vs t time. Now from these three equations, the variation of constants were studied with inlet SO_2 concentration, and thus a general empirical equation was found in terms of inlet SO_2 concentration and time to get outlet SO_2 concentration at that time and inlet concentration.

The results obtained are as follows-

6.5.1.1 GENERAL EQUATION OF CURVE WITH INLET SO_2 CONCENTRATION AS VARIABLE

(RH = 32%)

Space velocity = 1876/hr

Temperature = 120 °C

$$C/C_o = a + bt + ct^2 + dt^3$$

where,

$$a = -0.007782 + 0.101458 C_o - 0.098241 C_o^2$$

$$b = -0.013150 + 0.020519 C_o + 0.00093 C_o^2$$

$$c = 0.000845 - 0.000467 C_o - 0.00003 C_o^2$$

$$d = -0.000005 - 0.000001 C_o + 0.000002 C_o^2$$

6.5.1.2 GENERAL EQUATION OF CURVE WITH INLET SO_2 CONCENTRATION AS VARIABLE

(RH=41%)

$$C/C_o = a + bt + ct^2$$

where,

$$a = -0.054411 - 0.167279 C_o + 0.076812 C_o^2$$

$$b = 0.008767 + 0.021617 C_o - 0.006678 C_o^2$$

$$c = 0.000038 - 0.000220 C_o + 0.000060 C_o^2$$

6.5.2 GENERAL EQUATION OF CURVE WITH TEMPERATURE AS VARIABLE

$$C/C_o = a + bt + ct^2 + dt^3$$

where,

$$a = -0.393870 + 6.406169 T - 34.155399 T^2 + 65.481384 T^3$$

$$b = 0.282436 - 5.677510 T + 36.426384 T^2 - 74.637077 T^3$$

$$c = -0.000415 + 0.017269 T - 0.100540 T^2 + 0.219202 T^3$$

$$d = -0.000002 - 0.000046 T + 0.000179 T^2 - 0.000397 T^3$$

C/C_o = SO_2 fraction in test gas coming
out of bed

t = Time in minutes

C = Concentration of SO_2 at any time
in the gas coming out of bed

C_o = Inlet concentration of test gas

T = Temperature of reactor in $^{\circ}C$

In Table 6.5 a comparison of values obtained from equations and actual experimental data has been shown. The results are found to be in good agreement.

Table 6.5

Comparison Of Fractional SO₂ Removal By Empirical Equations
With Experimental Values

Temperature = 120 °C
 Space velocity = 1876/hr
 Relative humidity= 32%

Time minutes	SO ₂ Concentration		SO ₂ Concentration		SO ₂ Concentration	
	outlet/inlet		outlet/inlet		outlet/inlet	
	Co = 500ppm		Co = 1000ppm		Co = 1500ppm	
	Exp.	Values from values equations	Exp.	Values from values equations	Exp.	Values from values equations
5.0	0.02	0.0195	0.05	0.0452	0.03	0.0236
15.0	0.10	0.0964	0.18	0.1853	0.22	0.2296
30.0	0.32	0.3376	0.44	0.4546	0.52	0.5290
45.0	0.66	0.6336	0.76	0.7263	0.81	0.7803
60.0	0.86	0.8756	0.90	0.9230	0.95	0.9417
80.0	0.93	0.9271	0.96	0.9355	0.95	0.9454

6.6 RATE CONTROLLING STEP-

The difficulty in precisely determining any mechanism as the sole overall rate controlling step using data from the sand bed reactor, is related to the semi-batch characteristics of the experimental apparatus (the SO₂ flow is continuous over a batch of sorbent), which increases the probability of having different mechanism controlling the overall rate at different times (Jorgensen et al., 1987).

Relative to the gas film diffusion step, the dispersion of the

solid sorbent in an inert silica sand avoids both channeling and by-passing of the sorbent, enabling a uniform gas flow with well defined gas/solid contact. Assuming satisfactory dispersion of sorbent without significant agglomeration, the modified Reynold number is

$$Re = \frac{d_p \mu_p}{\mu(1-\phi)} = \frac{4.56 \times 10^{-2} \times 5.82 \times 10^{-3}}{1.9 \times 10^{-4} \times (1-0.46)} = 2.5867$$

Colburn's j-factor for mass transfer

$$j = 5.7 Re^{-0.78} = 2.716$$

The gas transfer number

$$k_g = j \times G/M \times Sc^{-2/3} \\ = 6.227 \times 10^{-4}$$

where,

G = Mass gas flow rate $\text{gm/cm}^2\text{-sec.}$

M = Gram molecular weight of air

A gas transfer number of 6.227×10^{-4} suggests a very fast mass transfer rate from gas to solid sorbent.

Time T , for complete reaction of a solid particle with a gas, assuming that gas film diffusion is rate controlling, can be expressed as (Levenspies, 1972)

$$T = \frac{\rho_p R}{3bk_g C_{Ag}} = 8.29 \text{ sec.}$$

where,

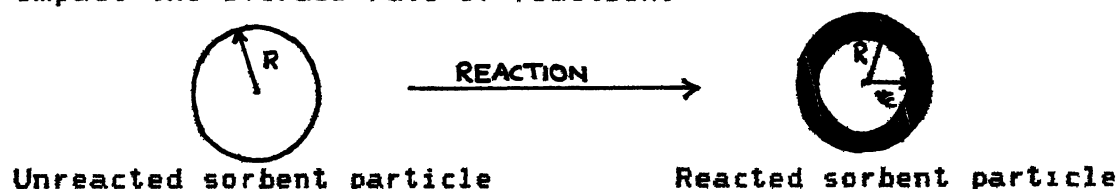
ρ_p = sorbent particle molar density, for
calcium silicate, mol/cm^3

R = sorbent particle radius, cm

b = reaction stoichiometry for CaSiO_3

C_{Ag} = bulk conc. of SO_2 in gas phase (1000ppm)

This suggests that 10 micrometer diameter particle would react totally with SO_2 in a matter of seconds if gas-phase diffusion were the overall rate controlling step. As the measured time for reaction is much longer (as will be seen, significant amounts of unconverted sorbent are found even after 100 min. reaction), gas film diffusion can probably be excluded as the overall rate controlling step. The results also indicate that the actual gas face velocity chosen would not impact the overall rate of reaction.



where,

R = radius of sorbent particle

r_c = radius of unreacted core

$$\text{Fraction conversion} = 1 - (r_c/R)^3$$

this gives $r_c/R = 0.923$ to 0.968

Such a high value of r_c/R suggest that most of the reaction takes place on the surface which, in turn, indicate the possibility of pore diffusion being the rate controlling step. A very low value of activation energy and order of reaction close to 1.0 also suggest the same,

7. SUMMARY AND CONCLUSION

From the foregoing studies the following conclusions may be drawn--

1. It was found that initial break through for SO_2 occurred quicker at higher SO_2 concentration. The percent utilization of sorbent was also observed to increase with the increase in SO_2 partial pressure in the test gas.
2. On humidifying the gas, the SO_2 removal increases, probably due to reduction in SO_2 diffusion resistance by water adsorbed on the sorbent particle.
3. With the increase in temperature (within the range studied), the SO_2 removal in packed bed with Calcium Silicate sorbent increases.
4. Order of reaction for $\text{CaSiO}_3/\text{SO}_2$ has been obtained very close to 1.0.
5. The activation energy (E) for $\text{SO}_2/\text{CaSiO}_3$ reaction was found to be 199.04 cal/mol. And the variation of rate constant with temperature in the Arrhenius form was found to be $k = 5614.77e^{(-E/RT)}$ (1/mol)/hr.
6. The data obtained from the generalized empirical equations for different variables have been found to reasonably corroborate with the experimental data.

8. SUGGESTIONS FOR FUTURE WORK

Based on the experimental program of this study, it is felt that further work should be pursued in the same field before such a process could be utilized under pilot scale testing and field testing. In the present work, calcium silicate was used as sorbent with the aim of using wollastonite rock which contains 99% of CaSiO_3 . So further experiments on Wollastonite should be conducted and reaction kinetics should be studied.

Studies on the effect of various additives (sodium nitrate, calcium nitrate, sodium chloride, calcium nitrate and sodium hydroxide etc.) on SO_2 removal should be carried out to get best possible additives.

The relative humidity of test gas could not be varied over wide and controlled range, due to unavailability of instruments. So experiment should be conducted for different values of relative humidity of test gas in order to find the relative humidity for maximum removal.

In the present study the experiments were run only at one space velocity. Efforts should be made to see the effect of space velocity on SO_2 removal.

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APPENDIX-A

CALCULATION OF SO₂ CONCENTRATION IN TEST GAS SAMPLE FROMABSORBANCE DATABARIUM SULFATE TURBIDITY METHOD (James, et al., 1989)

A1 = Initial absorbance at 500 nm against air as blank

A2 = Final absorbance reading at 40 minutes after adding BaCl₂

x = Microgram of sulfate in impinger (can be read from calibration curve Fig.5.1 corresponding to (A1-A2) reading)

In the present work 20 ml absorbing solution was used and sampling time was taken as 10 seconds.

Concentration of SO₂ in air sample (microgram)

$$= \frac{\text{Total no. of micro moles of Sulfate in impinger}}{\text{Air flow rate (lpm) * Sampling time (min.)}} \times 64062$$

$$\text{SO}_2 \text{ (ppm)} = \text{SO}_2 \text{ (microgram/cu.m)} \times 0.000382$$

Let for A2-A1 = 0.069 × 2

the corresponding sulfate from calibration curve = 327.75 microgram

$$\text{SO}_2 \text{ in microgram} = \frac{(327.75/96) \times 60}{2 \times 10} \times 64062 = 654673.6$$

$$\begin{aligned} \text{SO}_2 \text{ in ppm} &= 654673.6 \times 0.000328 \\ &= 214.73 \text{ ppm} \end{aligned}$$

APPENDIX-B

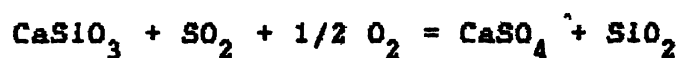
FEASIBILITY OF $\text{CaSiO}_3/\text{SO}_2$ REACTION

Feasibility of $\text{CaSiO}_3/\text{SO}_2$ reaction was checked by finding the Gibb's free energy.

At standard temperature and pressure, Gibb's free energies:

$G(\text{CaSO}_4)$	=	-313.52 Kcal/mol
$G(\text{SiO}_2)$	=	-192.40 "
$G(\text{CaSiO}_3)$	=	-357.80 "
$G(\text{SO}_2)$	=	-71.79 "

(Perry, et al., 1983)



$$G(\text{reaction}) = G(\text{formation of products}) - G(\text{formation of reactants})$$

$$\begin{aligned} G(\text{reaction}) &= -313.52 - 192.40 - (-357.80 - 71.79) \\ &= -76.33 \text{ Kcal} \end{aligned}$$

Since the Gibb's free energy is coming out to negative, therefore the reaction is feasible.

APPENDIX-C

Calculation For Percent SO_2 Removal, Conversion And Percent Utilis-

Utilisation of Sorbent

Following calculations are based on the breakthrough curve for inlet SO_2 concentration of 1000 ppm as shown in Fig.6.1 (All the measurements were taken at room temperature).

From Fig.A1 area above breakthrough curve (shaded portion) = 29.3 units
 Volumetric flow rate = 0.002 cu.m/min.

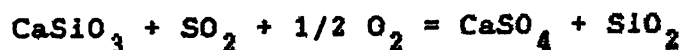
Total amount of SO_2 absorbed = $29.3 \times 0.002 \times 2617.6 \times 1000$ microgram
 = 0.1534 gm

(1 ppm SO_2 = 2617.6 microgram/cu.m SO_2 at STP)

Total amount of SO_2 supplied during 80 min.run
 = $80 \times 0.002 \times 2617.6 \times 1000$ microgram
 = 0.41882 gm

Percent SO_2 removal = $(0.1534/0.41882) \times 100$
 = 36.62%

Since 2 gm of CaSiO_3 was dispersed in 100 gm sand



1 mole of CaSiO_3 = 1 mole of SO_2
 i.e. 116 gm of CaSiO_3 = 64 gm of SO_2

Moles of CaSiO_3 used = $2.0/116 = 0.0172413$
 Moles of SO_2 used = $0.1534/64 = 0.002397$

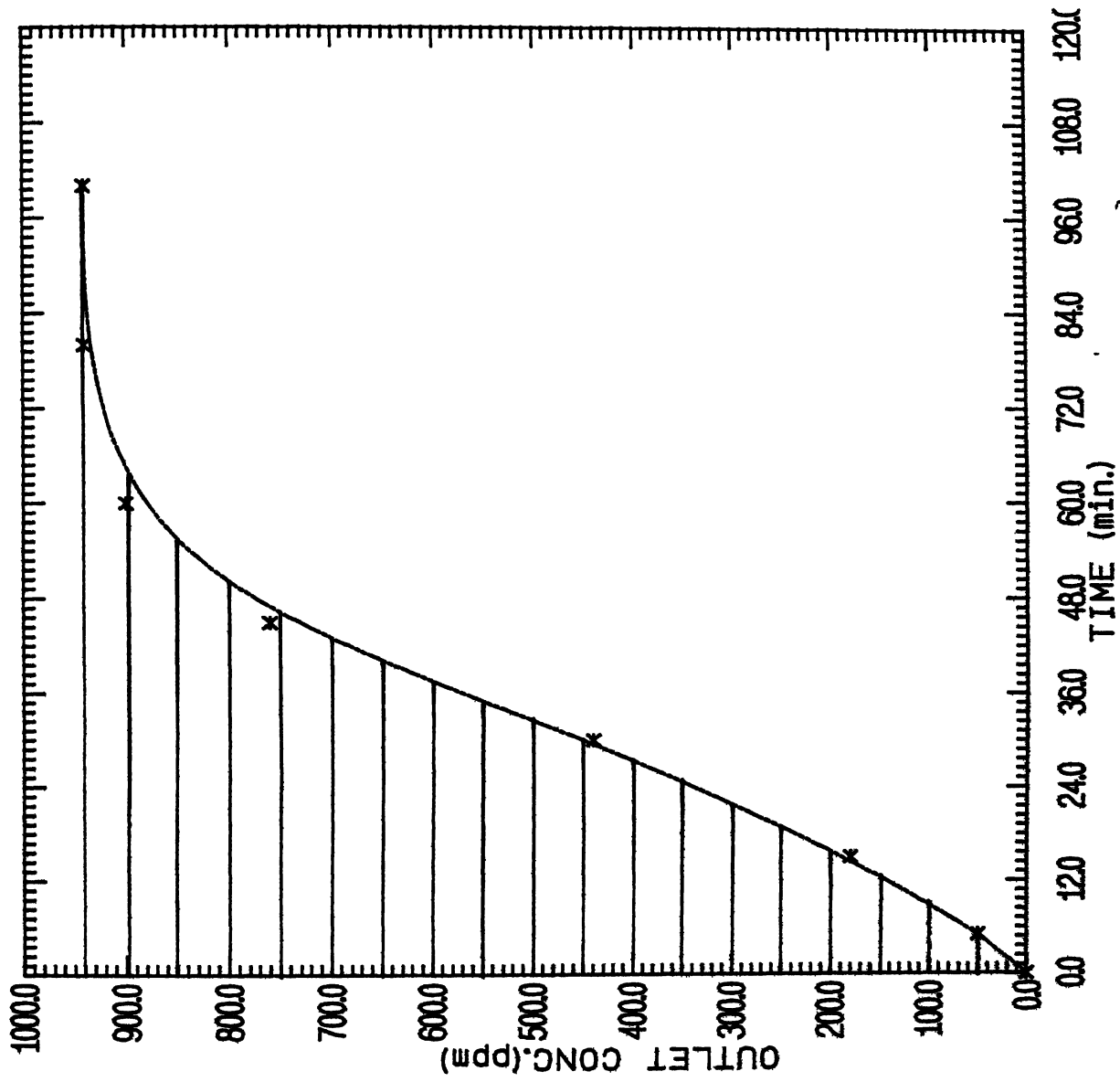


FIG.1 TYPICAL BREAK THROUGH CURVE FOR SO₂ USING CaSiO₃
 SORBENT IN SAND BED(TEMP.=120deg.C, SPACE VEL.=1876/hr, RH=41%)

Hence Conversion

$$\frac{\text{Moles of SO}_2 \text{ absorbed}}{\text{Moles of CaSiO}_3 \text{ used}} = \frac{0.002397}{0.0172413} = 0.139$$

$$\begin{aligned} \text{Percent Utilization of sorbent} &= (0.139/1.0) \times 100 \\ &= 13.9\% \end{aligned}$$

APPENDIX-D

SAND BED AS PLUG FLOW MODEL

Dispersion intensity was estimated by the method given in Levenspiel (1983).

$$\begin{aligned} \text{Reynold No. } Re &= \frac{d_p u \rho}{\mu} \\ &= \frac{5.5 \times 10^{-2} \times 5.82 \times 1 \times 10^{-3}}{1.9 \times 10^{-4}} = 1.685 \end{aligned}$$

$$\begin{aligned} \text{Schmidt No. } Sc &= \frac{\mu}{\rho D} \\ &= \frac{1.9 \times 10^{-4}}{1 \times 10^{-3} \times 0.156} = 1.2 \end{aligned}$$

where,

d_p = Particle diameter, cm

ρ = Gas density, g/cm³

μ = Gas viscosity g/cm-sec

D = SO₂ molecular diffusion
coefficient cm²/sec

From Fig.18 in Levenspiel corresponding to $Re = 1.685$ and $Sc = 1.2$

$$\begin{aligned} \frac{D_c}{\mu d_p} &= 0.320 \\ D &= \frac{0.320 \times 5.82 \times 5.5 \times 10^{-2}}{0.46} \\ &= 0.223 \end{aligned}$$

$$\begin{aligned} \text{Now Dispersion Number} &= \frac{D}{uL} \\ &= \frac{0.223}{5.82 \times 11.2} = 0.00342 \end{aligned}$$

This low dispersion number suggests that the effect of mixed flow probably can be disregarded and that a plug flow model is a reasonable assumption.

APPENDIX-E

FORTTRAN PROGRAM TO CALCULATE FRACTIONAL DEVIATION IN RATE CONSTANTVALUES

```
REAL N,D(4),XI(4),Y(4),YI(4),M,MI(4),M,K,KI(4),NI(50)
OPEN(UNIT=21,FILE='ar.d')
OPEN(UNIT=22,FILE='in.d')
XI(1)=8.62E-3
XI(2)=17.24E-3
XI(3)=25.86E-3
XI(4)=34.48E-3
NI(1)=0.8
NI(3)=1.1
NI(4)=1.2
NI(5)=1.3
NI(6)=1.4
NI(7)=1.5
NI(8)=1.6
NI(9)=1.7
NI(10)=1.8
NI(11)=1.9
NI(12)=2.0
COA=.0409
VO=3.33E-5
POR=.85185
DO III=1,4
READ(22,*)Y(III)
ENDDO
DO 99 II=1,12
N=NI(II)
DO I=1,4
```

```

YI(I)=1.0-(Y(I)**(1.0-N))
MI(I)=YI(I)/XI(I)
KI(I)=-MI(I)*VD/(POR*(N-1.0)*(COA**(N-1.0)))
ENDDO
SUMXY=XI(1)*YI(1)+XI(2)*YI(2)+XI(3)*YI(3)+XI(4)*YI(4)
M=SUMXY/8.92E-3
K=-M*VD/(POR*(N-1.0)*(COA**(N-1.0)))
DO I=1,4
D(I)=((KI(I)-K)**2.0)*100.0/(K*K*4.0)
ENDDO
DI=D(1)+D(2)+D(3)+D(4)
WRITE(21,*)N,DI,K
WRITE(*,*)N,DI,K
99 CONTINUE
STOP
END

```

A 11430

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date last stamped.**

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